LEVEL II

A METHOD FOR THE RAPID EVALUATION OF HAZARDS FROM TOXIC WASTE DEPOSITS,

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Growing public and governmental concern for the overall deterioration of the environment has led to laws regulating the release of potentially toxic materials into the air or water. However, the resulting pollution control processes also produce large quantities of potentially hazardous wastes. The Department of Defense, a leader in pollution control and site reclamation, is concerned about monitoring for the possible release of toxic components from wastes produced at installations engaged in explosives manufacturing, electroplating operations, chemical weapons demilitarization, etc. Toxic materials may be present in the liquid fraction of a waste, or in the leachate produced by rain or surface water percolating through a solid waste. As these solutions soak through the soil they eventually can reach the ground water and present a hazard to water users.

The migration of chemical substances through soil is usually determined in the laboratory using columns packed with soil to a predetermined bulk density. These soil columns are challenged with a solution extracted from a waste by water or some other solvent such as municipal landfill leachate, or the soil is treated with simple solutions of the ion under study. A useful configuration is shown in Figure 1, along with typical plots of the data obtained from continuously-leached columns. (This example illustrates the case where the concentration of the compound of interest is reduced by passing through the soil.) Besides requiring close attention to regulating flow-rate, an important limitation of continuously-leached column experiments is the time and effort required to obtain and analyze a sufficient number of samples to make predictions of migration rates and of the toxic hazards that could result from leaching the waste. This usually requires months and may even take years, depending upon the flow-rate of the leaching solution through the column. The information obtained from a
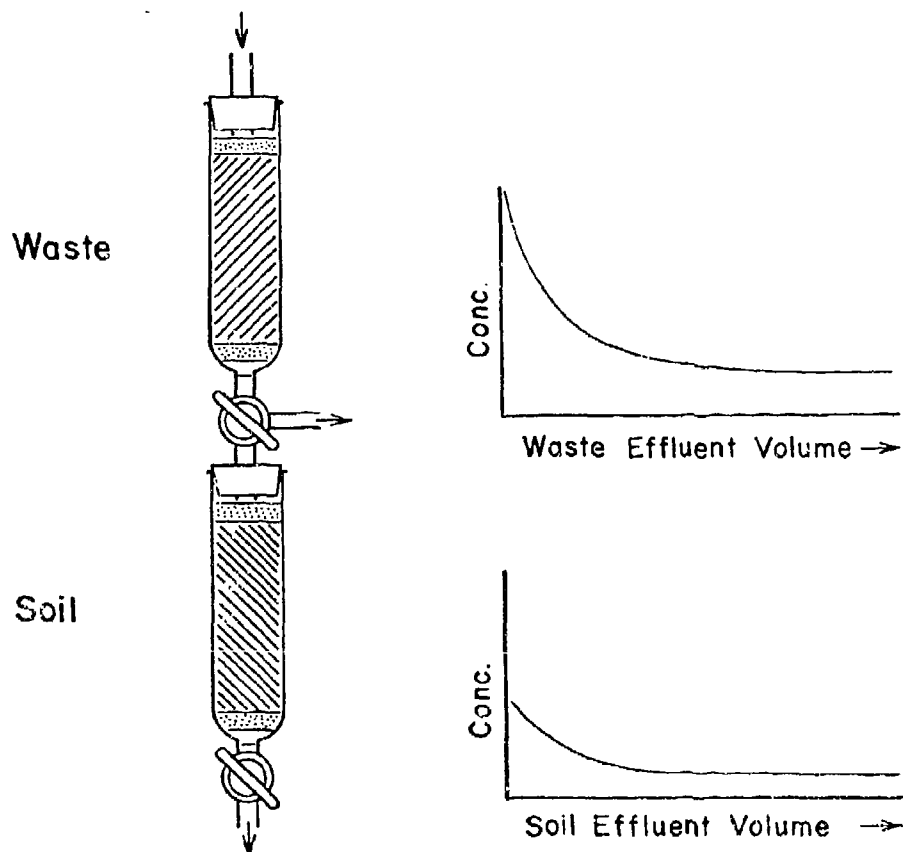
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Figure 1. Continuously-leached columns and associated output plots.

relatively short-term column study cannot be expected to describe what will occur during years of leaching.

An Army activity wishing to evaluate the potential hazard from the disposal of a waste is faced not only with the problem of obtaining valid results in a reasonable length of time but also with designing experiments that adequately represent the field situation. An investigator must select values for each experimental parameter such as leaching solvent flow-rate, head pressure, soil bulk density, column diameter, waste-to-soil ratio, leaching time, etc. The choice of these values may not all be entirely arbitrary, but a given set will yield results which probably apply only to that particular combination of conditions and the experiment may not be very useful for making general predictions of the migration of chemical compounds through soil.

By having a more rapid and flexible experimental approach, a wider range of conditions can be investigated within the framework of

factorial experiment designs which do allow making predictions even in the presence of statistical interaction between multiple variables. A fast method also allows making timely determinations, on demand, for each specific situation.

A graded serial batch procedure which is rapid and widely applicable has been developed in this laboratory. To validate this procedure, it first was necessary to establish a correlation between the batch procedure and continuously-leached columns. Experimental comparisons obtained were good and a consideration of the plotting parameters (discussed below) showed that this new approach could accelerate the testing of waste leachability and contaminant movement through soils.[1] The procedure also normalizes the results so they can be correlated to a range of field conditions. Some elements of this study have been corroborated by investigations conducted elsewhere.[2,3]

CORRELATING CONTINUOUS AND BATCHWISE LEACHING

The data obtained from continuously leached columns may be presented in several ways. One technique is to plot the concentration of the chemical of interest found in the waste or soil column sample versus the cumulative volume through the column. The common way of expressing the cumulative volume is to use the cumulative pore volume calculated for the type and weight of soil employed. (The pore volume is the interstitial void in a volume of soil, and the total void space depends upon soil type and mass.) The scale of the cumulative volume axis therefore changes for different soil types and sample sizes when pore volume is employed. Figure 2 is an example showing the difference obtained with pore volumes of 40 and 60 milliliters. The corresponding total volume in milliliters is appended for comparison.

It often is not practical or possible to determine a pore volume for a waste due to its physical form (heterogeneous suspension, liquid, etc). Using the soil column pore volume as the measure of liquid volume through the waste allows correlating the waste-column output with the soil-column results in a given set of experiments. However, instead of using the soil pore volume as the principle plotting parameter, it is much more flexible to plot the observed concentration of a chemical in an extract versus the cumulative milliliters of leaching solvent per gram of waste or soil. This makes the scaling independent of soil type, soil sample weight, and waste-to-soil ratio, and allows the direct comparison of many different designs of experiments. The area under the curve represents the total weight of a chemical extracted per gram of waste or soil.

Batchwise extractions can be related to continuously-leached columns by recognizing that continuous leaching is equivalent to running a series of discrete extractions spaced by the frequency of collecting the effluent sample. Figure 3 shows that the concentration of the periodic column samples can be plotted to represent the average for
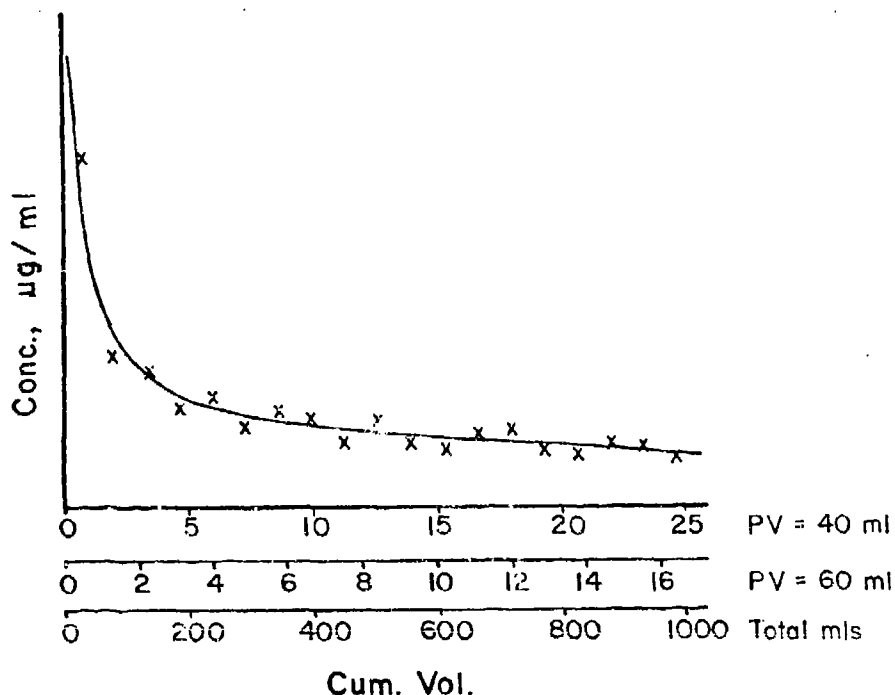
Figure 2. Differences in scales used to plot cumulative volume.

that sampling period. Thus, samples from the continuous leaching of a
column correspond to sequential batchwise extractions by volumes of
extractant equal to the volume passing through a column between the
taking of samples.

When extracting a batch of waste or soil, instead of using
the same volume of solvent for each successive extraction, the solvent-
to-waste or -soil ratios can be graded in size as indicated by the
extraction volumes pictured in Figure 4. A small solvent-to-solids
ratio should probably always be employed for the first extractions;
this is when the soluble species will be the most highly concentrated
in the extract and the ionic strength will be at its maximum. Greater
dilutions would reduce this, possibly affecting the solubility of other
components. After the more soluble components have been extracted, the
solvent-to-solids ratio can be greatly increased, thus reducing the
total number of extractions required. The further along the cumulative
milliliters per gram axis that the extraction volumes extend, the
longer the period of column leaching the batch work is equivalent to.

Since batch extractions are quite rapid compared to letting
the liquid percolate through a column, sequential batch extractions can
be the basis for accelerated testing of wastes and soils. By relating
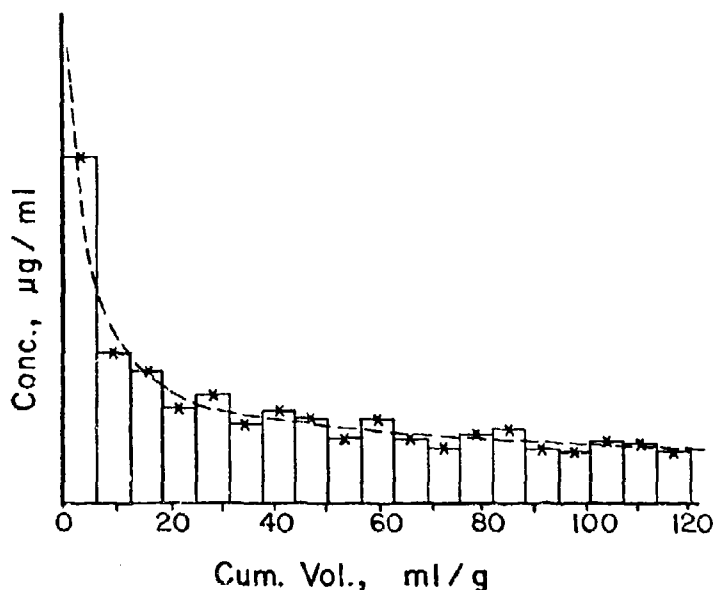
Figure 3. Relation between batch extractions and continuously-leached columns.

the rate of liquid-front movement to the volume flow rate per unit time, a scale of equivalent contact time can be added parallel to the axis labeled cumulative volume per gram, as shown in Figure 4. (The development of this concept is discussed in detail elsewhere.)[1] Table 1 lists the cumulative volume, in milliliters per gram, for the liquid-to-solid ratios employed, together with the equivalent exposure time for liquid front velocities of 1×10^{-4}, 10^{-5}, and 10^{-6} centimeters per second.

THE GRADED SERIAL BATCH EXTRACTION OF WASTES AND SOILS

The waste composition changes as components are leached from the waste. Each succeeding portion of extract will therefore generally have a different composition. Besides being challenged by a changing solution, the soil's ion-removal characteristics continually change with time as the soil becomes conditioned and loaded by the passage of waste extracts. Since each portion of waste is changed by passage through a segment of soil, the conditioning each succeeding segment of soil receives is different and each segment therefore may remove different proportions of the various ions present in the waste extract. So although the soil segments start out the same, in effect they become different soils due to the passage of the different waste extracts.

The soil removes ions from the waste, but the waste extract can also displace ions from the soil. In addition, soil can pick up a
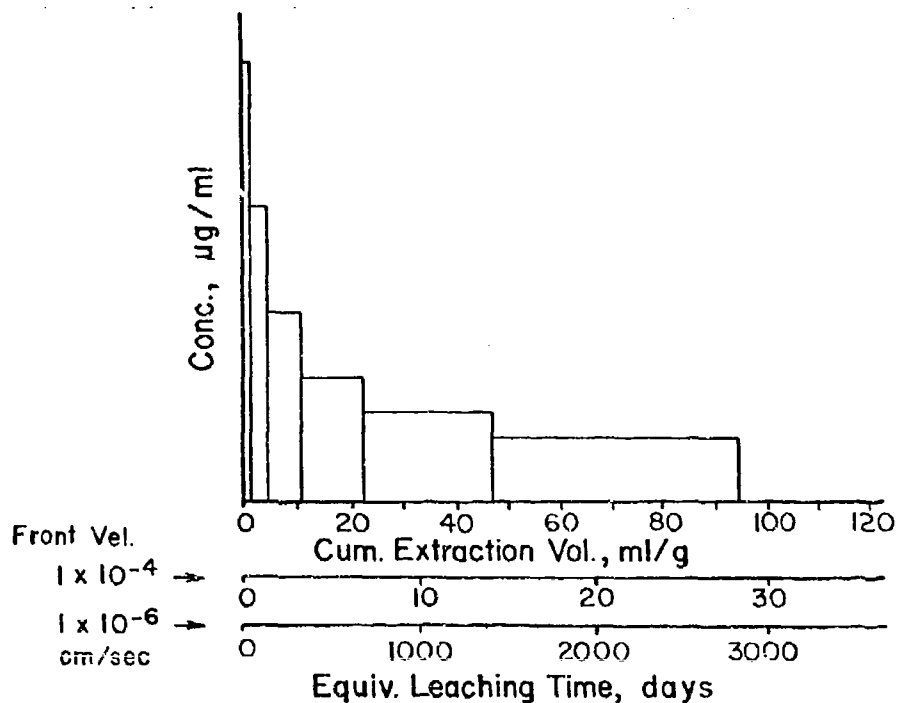
Figure 4. Relating extraction volumes to field leaching times.

TABLE 1.

Correlation Between Extraction Volume and Penetration Time

Extraction Number	Water Added, ml/g	Cumul ml/g	Equivalent Days of Penetration[a]		
			10^{-4}	10^{-5}	10^{-6} cm/sec
1	2	2	0.6	6	60
2	3	5	1.5	15	150
3	6	11	3.3	33	330
4	12	23	6.9	69	690 (1.9 yr)
5	24	47	14.1	141	1410 (3.9 yr)
6	48	95	28.5	285 (.78 yr)	2850 (7.8 yr)
7	96	191	57.3	573 (1.6 yr)	5730 (15.7 yr)

[a]At the specified liquid front velocity through a typical soil having bulk density of 1.6 g/cc and a pore volume of 0.24 ml/g.

specific ion from a waste solution of one composition and then give it up again as the liquid composition changes. The soil may also give up ions later because of intervening conditioning of the soil by the passage of the changing waste extract solution.

If extract samples were taken within a layer of soil, it would be possible to study this dynamically-changing situation. This can be accomplished by placing sampling ports in the side of a soil column, as shown in Figure 5. The same result can be attained in a shorter time with far fewer equipment difficulties by putting waste extracts on successive batches of soil and taking a sample after each extraction. A batch of soil then will represent a segment of soil from a soil layer.

Normally, the distribution of substances retained by the soil column is determined after leaching is conducted and the soil column is
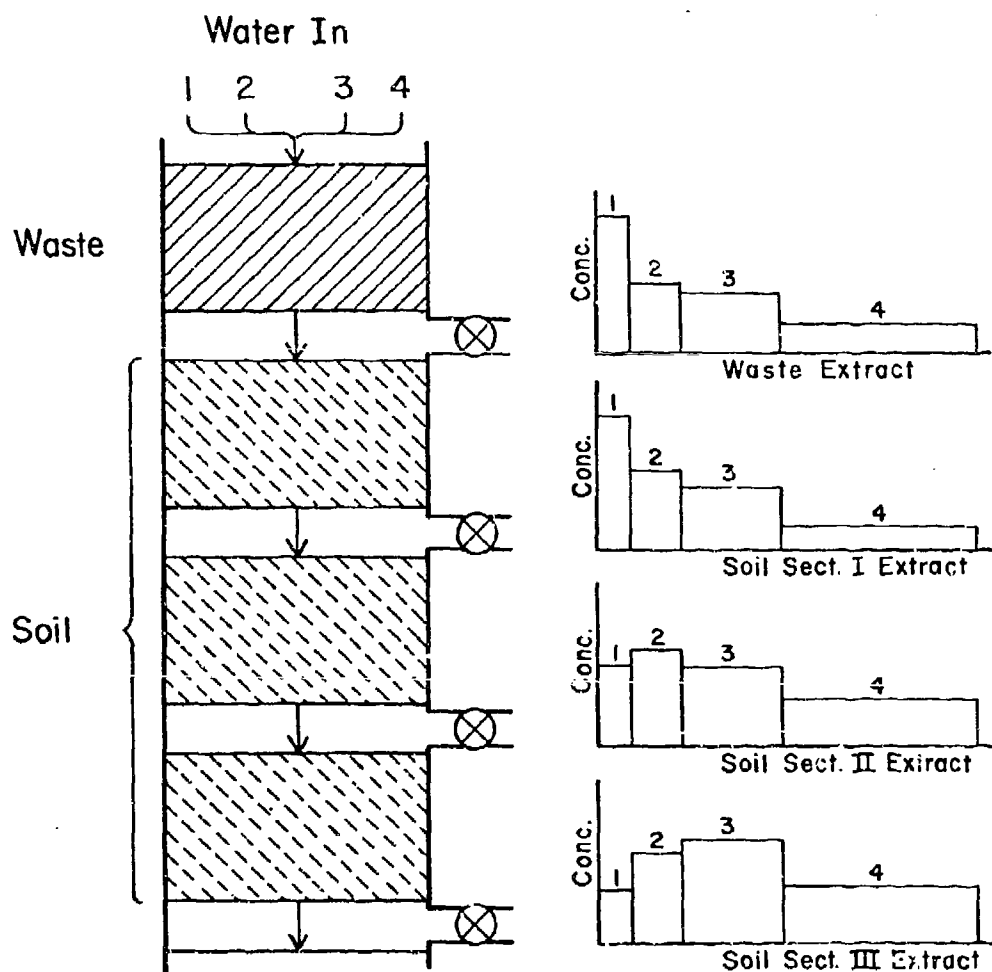
Figure 5. Challenging multiple soil segments with successive extracts of waste.

sectioned and analyzed. But, a serial batch approach, with sampling between batches of soil, yields a real-time picture of what is happening within a bed of soil and provides data which could allow extrapolating to the effect of thicker strata--something which cannot be done with validity from experiments with only a single layer, or from experiments which use artificially simple solutions. It is re-emphasized that batchwise testing also yields its information in a small fraction of the time required by columns or field studies.

THE EXPERIMENTAL PROCEDURE

A sequence of seven extracts was made from each type of industrial waste. First, a sample of waste was dried to determine moisture content, then sufficient undried sample to give 300 grams dry weight was weighed into a 2-quart, wide-mouth screw cap jar. (Drying the sample could affect hydrated species and drastically reduce the solubility. If the waste had supernatant water, the volume of the water was considered as part or all of the first extraction.) Appropriate volumes of water were added for each extraction to produce the liquid-to-solid ratio given in the second column of Table 2. The bottle was shaken gently four or five times each day. (Continual mechanical shaking was not used because of concern that it might abrade the waste agglomerates, making them more susceptible to extraction.) The time required to reach equilibrium can be determined by periodically withdrawing an aliquot for analysis; 24 hours is adequate for most wastes of small particle size. At the end of each extraction period, the mixture was filtered under vacuum using a hardened filter paper (such as Whatman 54) in a Buchner funnel. An aliquot of approximately 20

TABLE 2.
Specifications for Serial Batch Extractions

Extraction Number	Water Added, ml/g	Volume of Water, ml, Extracting 300 g Waste	Volume of Filtrate Onto a Soil		
			I 60 g Soil	II 30 g Soil	III 15 g Soil
1	2	600	120	60	30
2	3	900	180	90	45
3	6	1,800	360	180	90
4	12	3,600	720	360	180
5	24	7,200	1,400	720	360
6	48	14,400	2,800	1,400	720
7	96	28,800	5,760	2,280	1,440

milliliters was withdrawn for analysis and filtered through a 0.5 μ Millipore filter to remove fine particulates which might have bypassed the filter paper to possibly dissolve when the sample was acidified.

(After measuring conductance and pH, one percent concentrated nitric acid was added to inhibit precipitation while standing.) The solid waste residue was transfered back to the jar and mixed with the volume of water specified for the next extraction.

In the procedure detailed here, the liquid-to-solid ratio was continually increased to further accelerate the testing--the volume of each extraction after the second one was made double the one before, which redoubles the time represented by that extract. With some wastes adequate results may be obtainable from using very large volumes right from the first (or one or two extractions using small liquid-to-solid ratios, followed by a very large one) but this would have to be checked for each kind of waste. However, this procedure will allow rapid simulation of long leaching periods and could be useful in the routine monitoring of variations in waste composition and leachability.[4]

The filtrate resulting from each sequential extraction of the waste was mixed with the first of three batches of each kind of soil. The weights of soil used were 60, 30, and 15 grams, representing sections I, II, and III, respectively. This gradation in weight allows taking an aliquot of the extract for analysis and having enough left over to challenge the next soil batch with the same liquid-to-solid ratio. Extracting 300 grams of waste yields sufficient solution to challenge three different kinds of soil in experiments set up with the proportions stated in Table 2.

Although the soil equilibrates in 6 hours or less[5], each solution was kept in contact with the batch of soil before filtration for the same length of time as used to extract the waste. This was to keep the samples progressing smoothly without gaps in the series. After filtering the soil extract, an aliquot was refiltered through Millipore and saved for analysis. The appropriate volume of the remaining filtrate was added to the next batch of soil. The soil exposed to the first waste extract was recovered and mixed with the second waste extract in the series. This was repeated until the waste had been extracted seven times and each waste extract had progressed through all three soil batches. This procedure was run in duplicate.

APPLICATION OF THE BATCH TECHNIQUE TO INDUSTRIAL WASTES

Two industrial wastes of widely divergent characteristics were carried through a series of seven batch extractions. The resulting extracts were used to challenge three different kinds of soils. The extract samples were analyzed to determine the amount of each ion of interest, the pH, and the conductivity at every stage of the batch tests. In about two weeks of laboratory work with each waste, these experiments simulated approximately 1.6 years of leaching under field conditions that give a liquid front velocity of 1×10^{-5} cm/sec. An eighth extraction would have extended this to the equivalent of three years in the field. The composition of the wastes and soils are

detailed below, together with the interpretation of the experimental results.

WASTE COMPOSITION

a. Elemental Phosphorus Production Waste. This waste originated from the production of elemental phosphorus by the electric furnace method. First, the ore is dried and calcined in a kiln and gases containing phosphorus, fluorides, and fuel decomposition products are emitted. These gases are passed through a water scrubber and the resulting liquor is treated with lime to precipitate these compounds. The solid fraction of the waste is composed primarily of calcium phosphate, calcium fluoride, calcium sulfate, and unreacted lime. The species of interest in the waste leaching and soil migration study were inorganic phosphorus (probably present as phosphates) and fluoride. These anions were present in a slurry of high alkalinity (pH 12.7).

b. Zinc-Carbon Battery Rejects. This waste consists of broken-open reject batteries. (Approximately one percent of the batteries produced are rejected.) The extract samples were analyzed for the mercury, zinc, cadmium, and lead leached from the batteries. These cations were present in a solution only slightly above neutrality (pH 7.5).

c. Soil Composition. Three soils were investigated for their ability to remove the metals of interest from extracts of the two wastes. The soils chosen were Chalmers (a gray, silty, clay loam from Indiana, a Mollisol), Davidson (a red clay from North Carolina, an Ultisol), and Nicholson (a yellow silty clay from Kentucky, an Alfisol) These soils were selected because of differences in their chemical properties and clay mineralogy. Chalmers and Nicholson soils have similar surface areas but the higher percentage of clay in the Nicholson soils yields a higher cation exchange capacity. In addition, the clay mineral composition is much different. The Chalmers clay composition is largely montmorillonite, with very small amounts of vermiculite, chlorite, and kaolinite. The Nicholson clay fraction is predominately vermiculite with only a trace of mica and kaolinite. In contrast, Davidson soil has a low surface area and cation exchange capacity. The clay fraction is predominately kaolinite which has a significantly lower cation exchange capacity than the above clays but this soil contains a higher percentage of hydrous oxides of iron. It has been shown that iron oxides play a major role in heavy and trace metal removal.[6]

d. Interpretation of Results. Plotting the waste output as in Figure 5 shows the depletion of the waste with continued leaching. To show the effect of passing the waste extract through soil, the histogram of Figure 6 is more useful. It presents the results obtained from extracting a batch of waste and placing these solutions in succession on three batches of soil. (Multiplying the observed concentration in micrograms/milliliter by the individual batch extraction volume
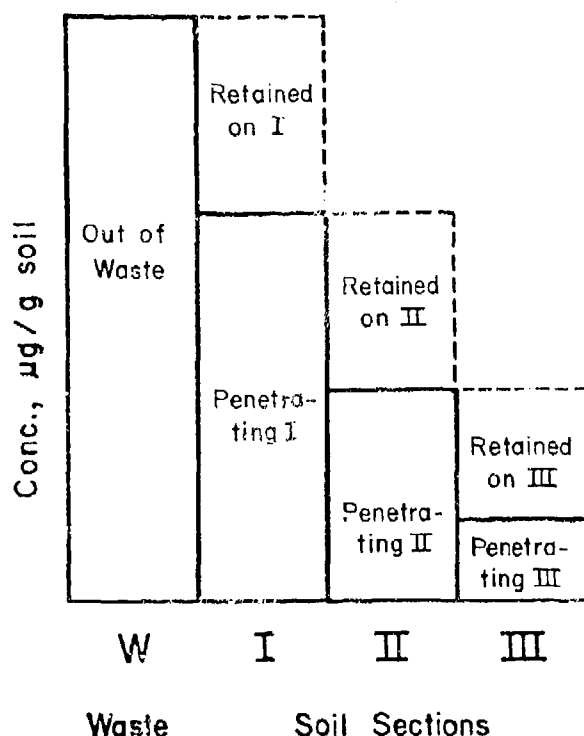
$$\text{Conc., } \mu g \,/\, g \text{ soil}$$

Figure 6. Histogram showing the pene-
tration and retention of a
species by soil.

per gram, milliliter/gram,
converts the values to micro-
grams/gram of waste or soil.)
The height of the histogram
bar labeled W represents the
micrograms of, e.g., phos-
phorus extracted per gram of
waste. This is the challenge
to the batch representing
soil section I. The height
of the bar labeled I shows
the concentration of phos-
phorus penetrating the batch
representing soil section I,
and the difference in height
between I and W is the amount
of phosphorus retained per
gram of soil. The ratio of
(W-I) to W is the fraction
removed by that soil section.
Similarly, I is the challenge
to II, and bar II shows the
penetration through II. If
the fraction of phosphorus
removed by each soil section
is different, this shows that
the removal characteristics
of the soil are affected by
conditioning and by changes
in the extract. This can be
further studied by comparing the histograms for the different extrac-
tions.

The soil batches can be treated in pairs as above, or it can
be considered that a given amount of waste has challenged three differ-
ent amounts of soil: section I, section I + II, and sections I + II +
III. Thus, the fraction removed can be calculated for three different
waste-to-soil ratios.

Because the fraction removed corresponds to the ratio of the
concentration in the soil to the concentration in the solution, this
is equivalent to the distribution coefficient, which is the slope of
the adsorption isotherm. By calculating the fraction removed for each
histogram bar, it is possible to follow the change in distribution
ratio (the change in slope of the adsorption isotherm) for each differ-
ent waste-to-soil ratio and for each serial extraction (which show the
effect of the changing sample matrix). This is of considerable

importance for modeling and for making predictions of contaminant movement through soils.

Figure 7 is a composite plot of histograms which show the extraction of inorganic phosphorus from phosphorus production waste and its penetration through Davidson and Nicholson soils. (Chalmers gave results similar to Davidson so it is not plotted here.) Although fluorine is also of interest in this waste, phosphorus is used here as the example. Because of space limitations, only four of the seven serial extractions are pictured. Going vertically down the figure viewing any single column shows how the extraction and penetration of phosphorus changes as the leaching progresses. For example, the W's show a continuous decrease in the phosphorus concentration in the waste extract as the leaching continues.

It is seen that neither soil is effective in removing inorganic phosphorus from this waste extract. (When the histogram bar is higher than the preceding one, it shows that the soil is releasing phosphorus.) Davidson is slightly more effective in retarding the phosphorus movement than is Nicholson soil, but the phosphorus appears to move through the soil as a zone similar to that obtained in elution chromatography. This is probably due to the high pH of the waste extract (the pH ranged from 12.7 to 11.6 in the four batches). This drastically changed the environment within most of the soil batches by changing the soil pH from slightly acid to strongly basic. This condition favors the mobility of anionic species.

The soils had a much different effect on the waste extract from the zinc-carbon batteries than on the phosphorus waste extract. Although several metal ions were found in significant concentrations in the battery waste leachate, zinc will be used here as the example. Figure 8 presents a composite plot of histograms giving the penetration of zinc in battery extract through Davidson and Nicholson soils. (Chalmers soil gave nearly the same results for zinc as did Davidson soil.) Both soils removed significant quantities of zinc from the waste extract, but Davidson soil is considerably more effective than is Nicholson soil. Although Nicholson soil has much higher surface area and cation exchange capacity than Davidson soil, the iron oxide content of the Davidson soil is much higher than the Nicholson. This is one of the important factors in removing zinc. The pH of the soil extracts was also affected. Even though the first waste extract had a pH of 7.6, the Nicholson soil extracts from batches I,II, and III were quite acid: pH 5.8, 4.5, and 4.7, respectively, for the first extract. In comparison, the first Davidson soil extracts were pH 6.4, 6.3, and 6.4. The pH of the extracts from both soils were not comparable until they had been exposed to the fourth waste extract. The ability of Nicholson soil to remove zinc began to approach the removal capability of Davidson soil by the fourth in the series of extractions, either because of a conditioning of the Nicholson soil or because the zinc is then present
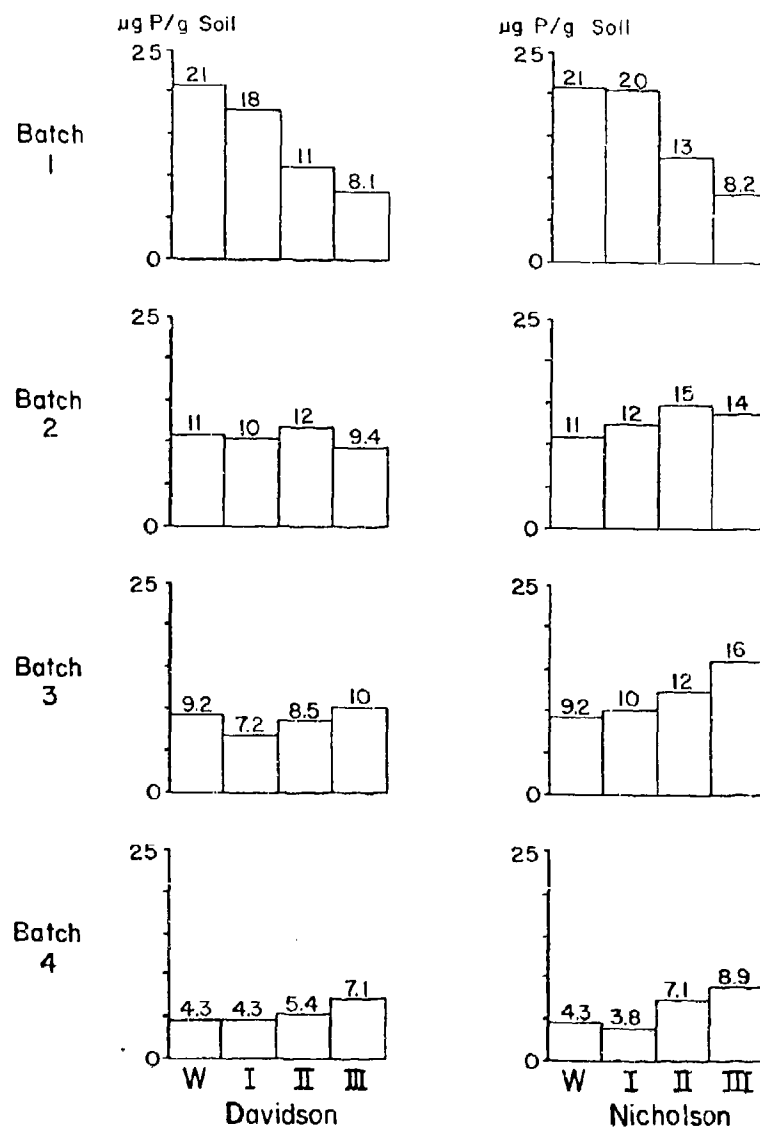
Figure 7.   The extraction and penetration through soils of inorganic
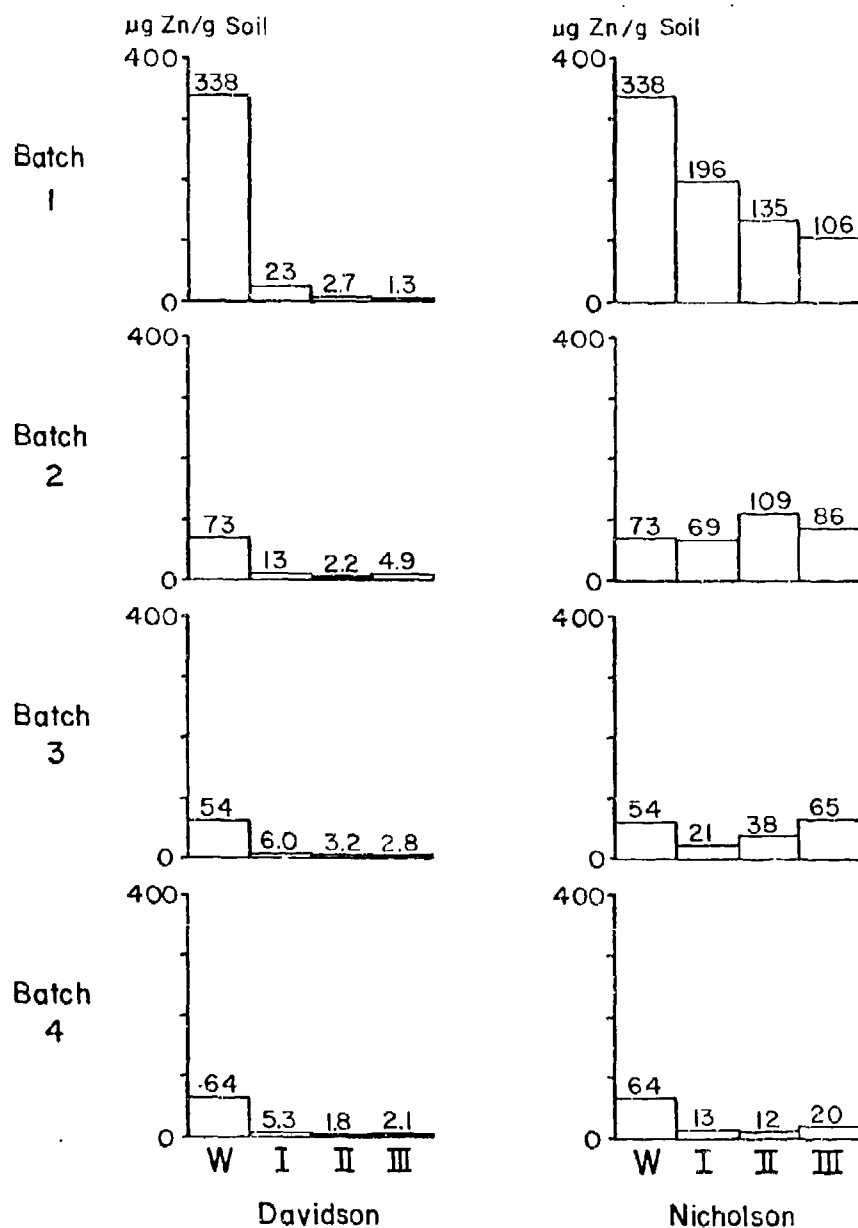phosphorus from phosphorus production waste.

Figure 8. The extraction and penetration through soils of zinc from
          zinc-carbon batteries.

in a waste leachate of different composition. Release of zinc from a soil section is shown whenever one histogram is higher than a preceding bar. Nicholson soil shows a considerable release of zinc from the second and third soil batches. This is probably zinc taken out of previous extracts but later released by the soil due to the change in composition of the later extracts and the different soil history.

CONCLUSION

It has been demonstrated that the leaching of a waste can be characterized and the ability of a soil to remove a chemical species from the waste leachate can be rapidly evaluated using serial batchwise extractions. This new method for evaluating a waste-soil system is not only much faster, it gives even more information than columns about the pickup and release characteristics of soils for toxic species in a dynamically changing situation. The batch technique is also far more convenient for rapidly investigating the effect of various environmental factors and lends itself to evaluating the effects of other variables such as sunlight, drying or freezing cycles, etc., via factorial experiments.

No one method can give all the answers, but the graded serial batch approach can quickly provide much of the information needed to assess the categories of hazards from a class of wastes and to make decisions concerning the suitability of soil types for inhibiting the migration of hazardous chemicals.

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